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REACTIVITY OF *ANTI*-O,O'-DIBENZENE RADICAL CATION IN ARGON MATRIX

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Neutral dibenzene **a** on standing at room temperature slowly cleaves into two molecules of benzene. In the case of the radical cation, other modes of rearrangement are considerable, like a cleavage of a single bond. However, after X irradiation of a sample kept at low temperature in an Ar matrix, a band at 920 nm is found, which is due to the dimer cation $(C_6H_6)_2^+$, **c**.

Calculations on possible intermediates and products of dissociation of $\mathbf{a}^{\cdot+}$ support the idea that the parent radical cation is instable under the condition of its generation. The reaction path is characterized by the initial scission of one bond between the two rings of **a** giving, with a barrier of few kcal/mol, the species **b** which relaxes, after a state crossing, to the dimer cation **c**. B3LYP/6-31G* method was used to map the energy profile of the process. Moreover, state diagrams were derived to depict how the relevant electronic states correlate along the dissociation path. For this case, all stationary points were recalculated at CASSCF(10,9) with an A.N.O. basis set, and dynamic correlation was introduced by the CASPT2 method.